Verification of Translation

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declare as follows:

1. That I am well acquainted with both the English and German languages, and
2. That the attached document is a true and correct translation made by me to the best of my knowledge and belief of the text of the **International Patent Application PCT/EP02/09107**.

19 January 2004
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(Date)

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(No witness required)

A substrate material for X-ray optical components

The invention relates to a substrate material for X-ray optical components, comprising a glass ceramic material with a thermal expansion $|\alpha|$ in a predetermined temperature range of $< 5 \times 10^{-6}\ K^{-1}$, a method for producing such a substrate material as well as the use of such a substrate material.

x-ray optical components are especially of particular interest in the field of X-ray lithography. This applies in particular to lithography with soft x-rays, i.e. the so-called EUV lithographies in the wavelength region of 10 to 30 nm. Mirrors with the highest possible reflectivity in the X-ray region are used as optical components in the field of X-rays. Such X-ray mirrors can be operated close to perpendicular incidence or in grazing incidence, namely as so-called normal or grazing incidence mirrors.

X-ray mirrors comprising a substrate and, based thereon, a multilayer system, namely so-called "Distributed Bragg Reflectors" (DBR), which will be referred to hereinafter as multilayers. They allow the realization of mirrors with high reflectivity in the X-ray region in the case of non-grazing incidence, i.e. in the normal incidence operation.

X-ray mirrors which are operated close to perpendicular incidence (normal incidence) are chosen over mirrors with glancing incidence (grazing incidence) which are covered with simpler layers in cases where high imaging quality by low aberrations is required, i.e. preferably in imaging systems such as projection lens systems for EUV lithography systems.

In order to increase the reflectivity of grazing incidence mirrors, the substrates of these mirrors can also be provided with a multilayer system.

Reference is hereby made to DE 199 23 609 A1 and the US Application Serial No. 09/322,813 as filed with the US Patent Office on 28 May 1999 under the title "reduction objective for extreme ultraviolet lithography" concerning projection lens systems for EUV lithography and related X-ray optical components, the scope of disclosure of which is hereby fully included in the present application.

Multilayer systems based on the substrate can be layer systems comprising Mo/Si, Mo/Be, MoRu/Be layer stacks with 40 to 100 layer pairs. Such systems lead in the EUV range λ_R = 10 to 30 nm to top-notch reflectivity in the region of 70 to 80%. Depending on the wavelength of the light to be reflected, layer systems of other materials can be used.

The high reflectivity of the layer stack is achieved by phase-adjusted superposition and constructive interference of the partial wave fronts reflected on the individual layers. The layer thicknesses must be checked typically in the region of less than 0.1 nm.

The necessary preconditions for the achievement of high reflectivity are sufficiently low layer and substrate roughness in the high spatial frequency roughness (HSFR) range. Depending on the approach, this spatial frequency range leads to loss of light by scattering outside of the image field of the lens system or by disturbance of the microscopically phase-correct superposition of the partial wave trains. The relevant spatial frequency range is downwardly delimited by the criterion of scattering outside of the image field and depending on the application it is typically at EUV wavelengths in the region of some µm. Generally, no limit is specified towards high spatial frequencies. A useful limit value lies in the range of half the wavelength of the incident light, because higher spatial frequencies are no longer seen by the incident photons. HSFR is usually measured with atomic force microscopes (SFM) which have the required lateral resolution.

Concerning the definition of HSFR, MSFR and fine surface figure error which is used in the following application, reference is hereby made to

U. Dinger, F. Eisert, H. Lasser, M. Mayer, A. Seifert, G. Seitz, S. Stacklies, F. J. Stiegel, M. Weiser, Mirror Substrates for EUV-lithography; progress in metrology and optical fabrication technology, Proc. SPIE Vol. 4146, 2000, the scope of disclosure of which is hereby fully included in the present application.

The fine surface figure error range according to the above publication reaches from the optically free diam ter, i.e. the aperture of the mirror, up to 1 mm of roughness wavelength. MSFR comprises the roughness wavelengths from 1 mm to 1 µm. The HSFR range comprises roughness wavelengths of 1 µm to 10 nm.

Other X-ray optical components may require a structure which is characterized by high reflectivity and low thermal expansion. Examples are a reticle mask for an EUV projection illumination system, a mirror with raster elements, so-called optical integrator or a collector mirror of an EUV illumination system. Reference is hereby made to DE 199 03 807 A1 and the US Application Serial No. 09/305,017 as filed with the US Patent Office on 4 May 1999 under the title "Illumination system particularly for EUV lithography", the scope of disclosure of which is hereby fully included in the present application.

Substrate materials for multilayer systems which are based on such materials are currently crystalline silicon, amorphous and semi-crystalline glasses such as the glass ceramic material ZERODUR® of Schott-Glas, Mainz.

In the field of high spatial frequency roughness (HSFR), a sufficient value of 0.1 nm rms for example can be achieved with classical superpolishing methods both on silicon as well as ZERODUR® and amorphous glasses. Since these methods lead at least in the aspheric regions generally to a deterioration of the fine surface figure error, i.e. defects in the low spatial frequency region, and in the mid spatial frequency roughness (MSFR) range to a deterioration of the long-wave shares in MSFR, it is usually necessary to provide a roughness-maintaining fine correction process after the superpolishing process.

Surface figure error and also the long-wave shares in MSFR (mm waves) can be brought to specification with beam processing methods, i.e. the IBF (ion beam figuring). The advantage of this method is that their tools can sit close so as to come to a snug fit especially on the typically aspheric surfaces. These beam processing methods are based on sputtering processing. The global and local sputtering rates depend on the physical and chemical bonding conditions in the solid body to be processed.

Whereas in single-crystalline silicon the additional energy introduction by the incident ions leads to a surface reorientation with the result of improved roughness, a slight deterioration of HSRF is observed in amorphous glass from approx. 0.06 to 0.15 nm rms. In semi-crystalline glass ceramic material like ZERODUR® for example with a

crystalline size of greater than 50 nm there was a serious deterioration from 0.1 to 0.4 nm rms.

Glass ceramic materials with a crystallite size of high quartz mixed crystals ≥80 nm and a mean coefficient of thermal expansion $a_{20°C-700°C} < 0.5 \cdot 10^{-6}/K$ are known from DE 199 07 038 A1.

Heat-resistant ceramic materials with a mean surface roughness ≤0.03 μm are shown by JP-A-04-367538. It does not make any statements concerning the mean thermal expansion. Furthermore, it makes no statements as to the spatial frequency range in which these roughness values are achieved.

Although the single-crystalline silicon is a suitable carrier under the aspect of the roughness requirements placed on the substrate material, it comes with mechanical anisotropy however and only allows for small mirror sizes due to its property as single crystal. Although the disadvantage of a coefficient of thermal expansion α which is higher than that of glasses can be compensated partly by a considerably higher thermal conductivity and suitable cooling, it still requires a high amount of technical effort. Silicon as a substrate is currently only considered in the case of very high thermal loads such as in illumination systems.

Although the thermal expansion and the roughness in the HSFR range are unproblematic when using amorphous glasses with low thermal expansion such as glasses as described in US 2,326,059, sufficient surface figure error and MSFR values cannot be reached because the lamellae-like striated structure of amorphous glass with negligibly low thermal expansion has a disadvantageous effect in these frequency ranges. As a result, these layers of a thickness of approx. 0.1 mm on moderately curved mirror surfaces lead to non-correctable surface modulations in the mm range with amplitudes of a number of nanometers far outside the values required for EUVL lithography. This effect is also observed in ion-beam-based production processes.

Although the semi-crystalline glass ceramic material ZERODUR® with crystallite sizes of greater than 50 nm has the desired low coefficient of thermal expansion, it leads to excessive roughness values in the HSFR range in the final beam processing process.

It is the object of the present invention to provide a substrate mat rial for X-ray optical components which has a low coefficient of thermal expansion like glass for example, but on the other hand ensures a sufficient surface quality of the X-ray optical components after the necessary surface processing steps.

The object of the invention is achieved by a glass ceramic material as a substrate material for X-ray optical components with an amorphous and a crystalline glass share. The glass ceramic material has a low coefficient of thermal expansion, the size of the microcrystallites is $< 4\lambda_R$, preferably $< 2\lambda_R$, especially preferably $< \lambda_R$, even more preferably $< 2/3\lambda_R$, especially $< \lambda_R/2$, with λ_R designating the mean wavelength of the incident X-rays. The substrate material in accordance with the invention still has sufficient roughness in the HSFR range after surface treatment, especially an ion beam figuring (IBF).

The inventors have surprisingly determined that certain glass ceramic materials fulfill all requirements concerning thermal expansion and surface properties. Such materials are stated in the following table 1.

Table 1: Glass ceramic materials and roughness

Glass ceramic material	Crystal size	HSFR before beam processing	HSRF after beam processing
CLEARCERAM Z ® (Ohara Co.)	38 nm	0.13 nm	0.24 nm
KERALITE ® (Eurokera Co.)	35 nm	0.10 nm	0.23 nm

The materials have a crystallite size of 35 nm (KERALITE ® of Eurokera Co.) or 38 nm (CLEARCERAM Z ® of Ohara Co.). The HSFR, i.e. the roughness in the roughness wavelength range of 1 µm to 10 nm is 0.13 prior to beam processing and 0.24 nm after the beam processing (CLEARCERAM Z ®) and 0.10 nm prior to beam processing and 0.23 nm after beam processing (KERALITE ®). Reference is hereby made to US 5,591,682 concerning the composition of CLEARCERAM Z ® of Ohara Co. and and to US 5,070,045 concerning the composition of KERALITE ® of Eurokera Co., the scope of disclosure of which is hereby fully included in th present application.

A normal-incidence X-ray mirror with a substrate material in accordance with the invention for EUV lithography is characterized by a favorable fine surface figure error, i.e. defects in the low spatial frequency region. This is typically understood as being structural sizes of between one-tenth of the ray bundle cross sections associated to the individual pixels up to the free diameter of the mirror, i.e. the defects lie in the magnitude of millimeters up to several decimeters. Such defects lead to aberrations and reduce the imaging precision and restrict the resolution limits of the system. With the components in accordance with the invention it is possible to achieve fine surface figure error values in the region of $\lambda_R/50$ to $\lambda_R/100$. In the EUV range, i.e. at wavelengths of 10 to 30 nm, this corresponds to 0.1 to 0.2 nm for 10 nm of wavelength and 0.3 to 0.6 nm rms for 30 nm wavelength.

They are further characterized by low roughness in the middle spatial frequency range (MSFR). These spatial wavelengths lead to light scatter within the image field (flare) and thus to losses in contrast for the imaging lens systems. The errors in the MSFR region can be estimated from formulas for TIS (total integrated scatter). With the invention it is possible to achieve defects in the region of 0.1 to 0.2 nm in EUVL applications.

Normal-incidence X-ray mirrors are also characterized by a low thermal expansion. This is important for EUV applications, because approximately 30% of the incident light is absorbed by the multilayer mirrors and is converted into heat. In order to ensure that the surface shape remains in a stable condition under these thermal loads in operation, a material with the lowest possible coefficient of thermal expansion is required in the imaging lens systems. Low coefficients of thermal expansion also contribute to the achievable dimensional precision in heat-producing processing processes.

The roughness of the X-ray optical components in the high spatial frequency roughness (HSFR) range is < $\lambda_R/30$ rms, preferably < $\lambda_R/50$ rms, especially preferably < $\lambda_R/100$ rms. At the same time the defect in the low spatial frequency range (which is the fine surface figure error range) is in the region of $\lambda_R/50$ - $\lambda_R/100$ rms and the roughness in the middle spatial frequency region (MSFR) lies simultaneously in the region $\lambda_R/50$ - $\lambda_R/100$ rms. At an EUV wavelength of 13 nm this corresponds to a roughness of 0.26 nm to 0.13 nm. The advantage of the substrate material in accordance with the invention is therefore that the roughness values lie in the different frequency ranges (fine surface figure error, MSFR, HSFR) in the region of 0.26 nm to 0.13 nm for EUV wavelengths.

In a first embodiment the X-ray optical component is reticle mask operated in reflection for the EUV lithography, comprising a substrate material in accordance with the invention.

In an alternative embodiment the X-ray optical component is a normal-incidence mirror, with the mirror having a substrate comprising a glass ceramic material as well as a multilayer system with a plurality of layers with high reflectivity in the X-ray range at non-grazing incidence.

Preferably, the multilayer system of the normal incidence mirror which is based on the substrate comprises 40 to 200 layer pairs which consist of one of the following materials: Mo/Si, Mo/Bi, MoRu/Be.

In addition to the glass ceramic material, the invention also provides a method for producing an X-ray optical component for X-rays of wavelength λ_R, comprising the following steps: The surface of the X-ray optical component is superpolished until a high spatial frequency roughness (HSFR) < $\lambda_R/50$ rms, preferably < $\lambda_R/100$ rms, is achieved. Thereafter the surface is further processed with a beam processing method until the defect in the low spatial frequency region is $\lambda_R/50$ - $\lambda_R/100$ rms and the defect in the middle spatial frequency region (MSFR) is $\lambda_R/50$ - $\lambda_R/100$ rms. The materials in accordance with the invention are characterized in that HSFR does not deteriorate substantially after beam processing, but that even after completion of this processing step an HSFR < $\lambda_R/50$ rms, preferably < $\lambda_R/100$ rms, is achieved.

The superpolishing of samples is well known to the person skilled in the art and superpolished samples can be purchased commercially.

Concerning the beam processing method of ion beam figuring (IBF), i.e. ion beam processing, reference is hereby made to L. Allen and H.W. Romig, "Demonstration of ion beam figuring process" in SPIE Vol. 1333 (1990) 22; S.R. Wilson, D.W. Reicher, J. R. McNell, "Surface figuring using neutral ion beams", Advances in Fabrication and Meterology for Optics and large Optics, SPIE, Vol. 966, p. 74-81, August 1988, as well as L.N. Allen and R.E. Keim, "An ion figuring system for large optic fabrication", Current developments in Optical Engineering and Commercial Optics, SPIE, Vol. 1168, p. 33-50,

August 1989, the scope of disclosure of which is hereby fully included in the present application.

During the surface processing with ion beam figuring (IBF), an Ar^+ beam is guided in a controlled manner over the surface of the substrate to be treated in vacuum by means of a 5-axis motion system. Based on a surface defect profile obtained by means of an interferometer for example, the dwell time of the processing beam is varied in a computer-controlled fashion depending on location. The excavation rate of the beam is proportional to the dwell time. As a result, the processing process is defined which converges rapidly within the stated boundaries. Details in connection with this method can be obtained from the above publications.

In the glass ceramic substrate materials, microcrystallites with negative thermal expansion are embedded in amorphous material with positive thermal expansion. During the crystallization phase the stoichiometric ratio of crystal to glass phase is set in such a way that there is a negligible thermal expansion for a specific temperature range, e.g. 0 to 50°C. The size of the crystallite is a free parameter. The inventors have recognized that for the purpose of achieving a negligible thermal expansion in first approximation it is irrelevant whether many small or a few large crystallites are embedded as long as the volume ratio of crystallite to glass remains constant.

The substrate materials in accordance with the invention have crystallite sizes in the magnitude of the wavelength of the incident light, preferably under half the wavelength.

The inventors have realized that the roughness amplitudes or degradations as induced by ion bombardment scale with the crystallite size. A tolerable degradation is achieved on EUV mirrors with the substrate materials in accordance with the invention after the surface processing, especially beam processing, which degradation is by a factor 3 to 4 times lower than in the case of glass ceramic materials with microcrystallites in the magnitude of 50 nm for example.

The substrate materials in accordance with the invention show roughness in all spatial frequencies (HSFR, MSFR, fine surface figure errors) after the surface treatment in a region which is no longer noticed by the X-ray photons. They can therefore no longer contribute to the reduction of reflectivity.

CLAIMS:

1. A substrate material for X-ray optical components for X-rays of wavelength λ_R, comprising a glass ceramic material with a glass phase made of amorphous material and a crystal phase, comprising microcrystallites, with the amorphous material having a positive thermal expansion and the microcrystallites having a negative thermal expansion and the stoichiometric ratio of crystal to glass phase being set in such a way that the amount of the thermal expansion α of the glass ceramic material is in a temperature range of 20°C to 100°C $< 5 \times 10^{-6}\ K^{-1}$, especially $< 1 \times 10^{-6}\ K^{-1}$, with the mean size of the microcrystallites being $< 4\ \lambda_R$, especially $< 2\ \lambda_R$, preferably $< \lambda_R$, more preferably $< 2/3\ \lambda_R$, especially $< \lambda_R/2$, characterized in that the substrate material, following a surface treatment, shows a roughness in the high spatial frequency (HSFR) region of $< \lambda_R/30$ rms, preferably $< \lambda_R/50$ rms, especially preferably $< \lambda_R/100$ rms.

2. A substrate material as claimed in claim 1, characterized in that the wavelength of the X-rays is in the range of λ_R of 10 to 30 nm.

3. A substrate material as claimed in one of the claims 1 to 2, characterized in that after a surface treatment the defect in the low spatial frequency region is in the range of $\lambda_R/50$ to $\lambda_R/100$ rms.

4. A substrate material as claimed in one of the claims 1 to 3, characterized in that after a surface treatment the defect in the middle spatial frequency region (MSFR) is in the range of $\lambda_R/50$ to $\lambda_R/100$ rms.

5. A substrate material as claimed in one of the claims 1 to 4, characterized in that in the surface treatment of the substrate material the surface of the X-ray optical component is superpolished at first and thereafter the surface is further processed by a beam processing method.

6. A substrate material as claimed in one of the claims 1 to 5, characterized in that the substrate material is a substrate material for a reticle mask for EUV

lithography.

7. A substrate material as claimed in one of the claims 1 to 5, characterized in that the substrate material is a substrate material for a normal-incidence mirror, with a multilayer system with a plurality of layers with high reflectivity in the X-ray range in the case of non-grazing incidence being applied onto the substrate material.

8. A substrate material as claimed in claim 7, characterized in that the mirror has an aspherical shape.

9. A substrate material as claimed in claim 7 or 8, characterized in that to the substrate material there is applied a multilayer system comprising 40 to 200 layer pairs consisting of one of the following materials:
Mo/Si
Mo/Bi
MoRu/Be.

10. An X-ray optical component, characterized in that it comprises a substrate material according to one of the claims 1 to 9.

11. An X-ray optical component as claimed in claim 10, characterized in that the X-ray optical component is a normal-incidence mirror or a grazing-incidence mirror.

12. An X-ray optical component as claimed in claim 10, characterized in that the X-ray optical component is a reticle mask.

13. A method for producing a substrate material for an X-ray optical component for X-rays of wavelength λ_R, with the substrate material being a glass ceramic material and the method comprising the following steps:

13.1 surface of the substrate material is superpolished until a high spatial frequency roughness (HSFR) of < $\lambda_R/30$ rms, preferably < $\lambda_R/50$ rms, even more preferably < $\lambda_R/100$ rms, is achieved;

13.2 the surface is further processed with a beam processing method until the defect in the low spatial frequency region is $\lambda_R/50$ - $\lambda_R/100$ rms and the defect in the middle spatial frequency region (MSFR) is $\lambda_R/50$ - $\lambda_R/100$ rms, with the high

spatial frequency roughness (HSFR) obtained being < λ_R/30 rms, preferably < λ_R/50 rms, even more preferably < λ_R/100 rms.

14. The use of a substrate material for X-ray optical components as claimed in one of the claims 1 to 9 in an EUV projection system, comprising an illumination system and a projection lens system.

15. The use of a substrate material for X-ray optical components as claimed in one of the claims 1 to 9 in one of the following fields:
X-ray microscopy;
X-ray astronomy;
X-ray spectroscopy.